2-(Trifluoroacetyl)imidazoles, 2-Trifluoroacetyl-1,3-thiazoles, and 2-Trifluoroacetyl-1,3-oxazoles

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Dedicated to Prof. A. M. Pinchuk on the occasion of his 70th birthday

Abstract: A facile method of trifluoroacylation of imidazoles, 1,3-thiazoles, and 1,3-oxazoles with trifluoroacetic anhydride resulted in a set of heterocyclic trifluoromethyl-containing ketones. Unlike common ketones, these compounds form stable hydrates and enter into noncatalytic ene reactions with terminal olefins affording the corresponding allyl alcohols.

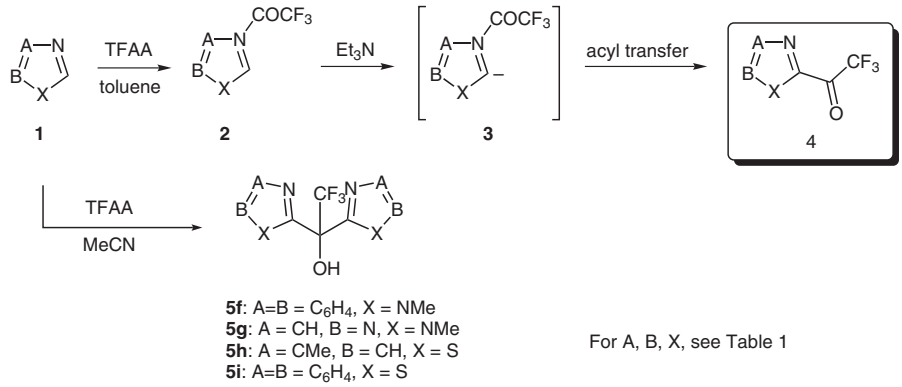
Key words: fluorine compounds, acylations, ketones, nitrogen-containing heterocycles, stable hydrates

Highly reactive trifluoromethyl ketones[1] such as hexafluoroacetone and trifluoropyruvates have been widely employed as electrophilic reagents for the modification of various biologically active compounds with trifluoromethyl groups.[2] Due to the influence of two strong electron-withdrawing groups, the chemical reactivity of these compounds differs from that of common ketones. For example, they show extremely high activity in the reactions with various nucleophiles and form stable hydrates,[2b,3] semiketals,[2b,4] and semiaminals[5] upon the addition of water, alcohols, and aliphatic amines, respectively. Their hydrolytically unstable Schiff bases rearrange into C-oxyalkylation products on heating;[6] and undergo ene[7] and Baylis–Hillman reactions.[8] Hexafluoroacetone also oxidizes alcohols in noncatalytic Meerwein–Ponndorf reactions.[9]

The reactivity of more complicated trifluoromethyl ketones bearing electron-acceptor heterocyclic fragments at the carbonyl group has not been studied systematically. Although a few hetaryl trifluoromethyl ketones have been obtained, their chemical properties have remained virtually unexplored.[10] The 2-, 3-, and 4-(trifluoroacetyl)pyridines form stable *gem*-diols;[10d] this indicates their high electrophilicity and potential applicability for the synthesis of various trifluoromethyl-containing compounds.

We report here on facile methods for the synthesis of various hetaryl trifluoromethyl ketones and on an exploration of their chemical properties.

Regel–Büchel acylation,[10a] phosphorylation, and silylation[11] of imidazoles, 1,3-thiazoles, and 1,3-oxazoles with acid chlorides (Et_3N, apolar solvent) occur at the *meso*-position to give the corresponding acylated derivatives in preparative yields. In the present study we utilize this synthetic approach for the acylation of imidazoles, 1,3-thiazoles, and 1,3-oxazoles **1** with trifluoroacetic anhydride, to prepare 2-(trifluoroacetyl)imidazoles, -1,3-thiazoles, and -1,3-oxazoles **4** (Scheme 1). The acylation of



Scheme 1

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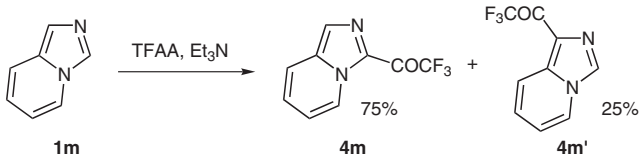
azoles **1** occurs according to a postulated mechanism[10a,12] via the intermediate heterocyclic ylide **3** (Scheme 1).

The least electron-accepting imidazoles **1a–d** and **1f** were acylated at –19 °C (Et_3N, toluene) to give the corresponding trifluoromethyl ketones **4a–d**,**f** in 75–89% yield (Scheme 1, Table 1, entries 1–4, 6). The addition of trifluoroacetic acid anhydride to **1a–d** and **1f** resulted in the precipitation of salts **2**, which dissolved upon the addition of triethylamine (Scheme 1).

The acylation of compounds **1f** and **1i** in acetonitrile gave ketones **4f** and **4i** as well as 2,2,2-trifluoro-1,1-bis(hetaryl)ethanols **5f** and **5i** (Scheme 1). The latter compounds appear to be formed by the reactions of intermediates **3f** and **3i** with the corresponding ketones **4**. It seems likely that the high polarity of acetonitrile facilitates this reaction through the stabilization of bipolar ylides **3**. The yields of compounds **5** can be increased to up to 78% by reversal of the order of addition of trifluoroacetic anhydride and triethylamine.

The acylation of imidazo[1,5-*a*]pyridine (**1m**) is complicated by acylation at position 1 affording 1-(trifluoroacetyl)imidazo[1,5-*a*]pyridine (**4m′**) (Scheme 2).[12a] However, the yield of the target product **4m** was increased to 75% if the reaction was carried out at –19 °C.



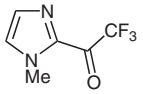
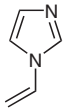
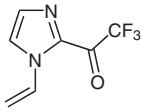
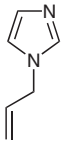
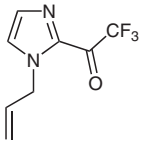
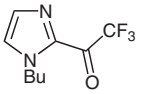
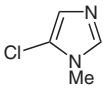
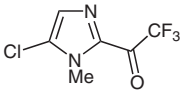
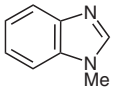
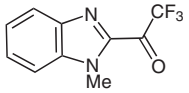
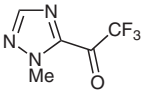
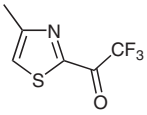
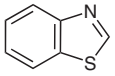
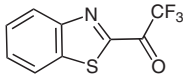
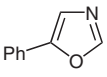
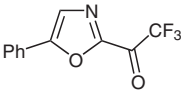
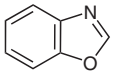
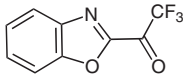
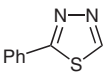
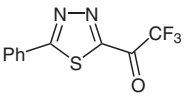
Scheme 2

The acylation of tetrazole gave an inseparable mixture of unidentified products, most probably because of the extrusion of nitrogen from the intermediate ylide. This is confirmed by evolution of gas after the addition of triethylamine to the reaction mixture.

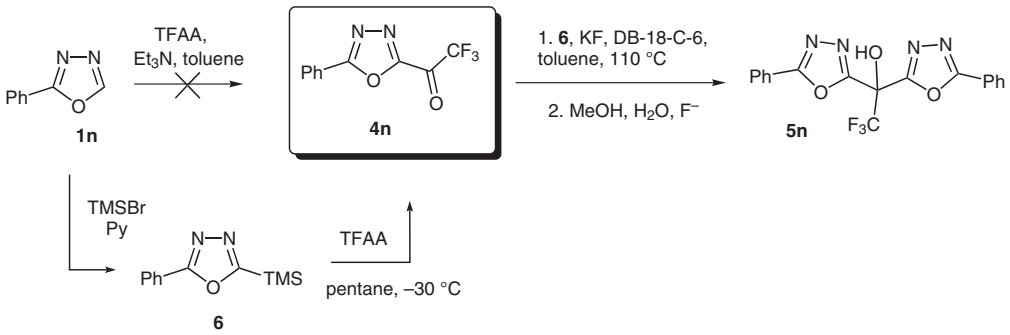
The acylation of oxadiazoles also failed (Scheme 3), probably because of the electron deficiency at the nitrogen atom, which hampers the N-acylation with trifluoroacetic anhydride, which is a first step of the acylation at position 2. This problem could be circumvented by the use of less electron-deficient and more reactive trimethylsilyl derivative **6**[11e] as starting material (Scheme 3).

Ketones **4** react with water to form stable hydrates **7** (Scheme 4). According to ^{19}F NMR spectroscopic studies of samples of hydrates **7** in aqueous solutions and wet organic solvents, the stability of the hydrates strongly depends on the electron-withdrawing ability of the heterocyclic unit. In the case of the least electrophilic imidazole derivatives **4a–d** (Table 1, entries 1–4), the hydration degree was found to be 35–40%, whereas **4e** and **4f** (Table 1, entries 5 and 6) are hydrated by 65% and 75%, respectively. Highly electrophilic ketones **4g–l**,**n** are completely hydrated in aqueous solutions.

Table 1 Structures and Yields of Hetaryl Trifluoromethyl Ketones **4**

Entry	Starting material **1**	Product **4**	Yield[a] (%)
1	 **1a**	 **4a**	82[10a]
2	 **1b**	 **4b**	75
3	 **1c**	 **4c**	85
4	 **1d**	 **4d**	77
5	 **1e**	 **4e**	83
6	 **1f**	 **4f**	89
7	 **1g**	 **4g**	65
8	 **1h**	 **4h**	72
9	 **1i**	 **4i**	99
10	 **1j**	 **4j**	80
11	 **1k**	 **4k**	65[10b]
12	 **1l**	 **4l**	56

[a] Yields refer to isolated and purified product **4**.

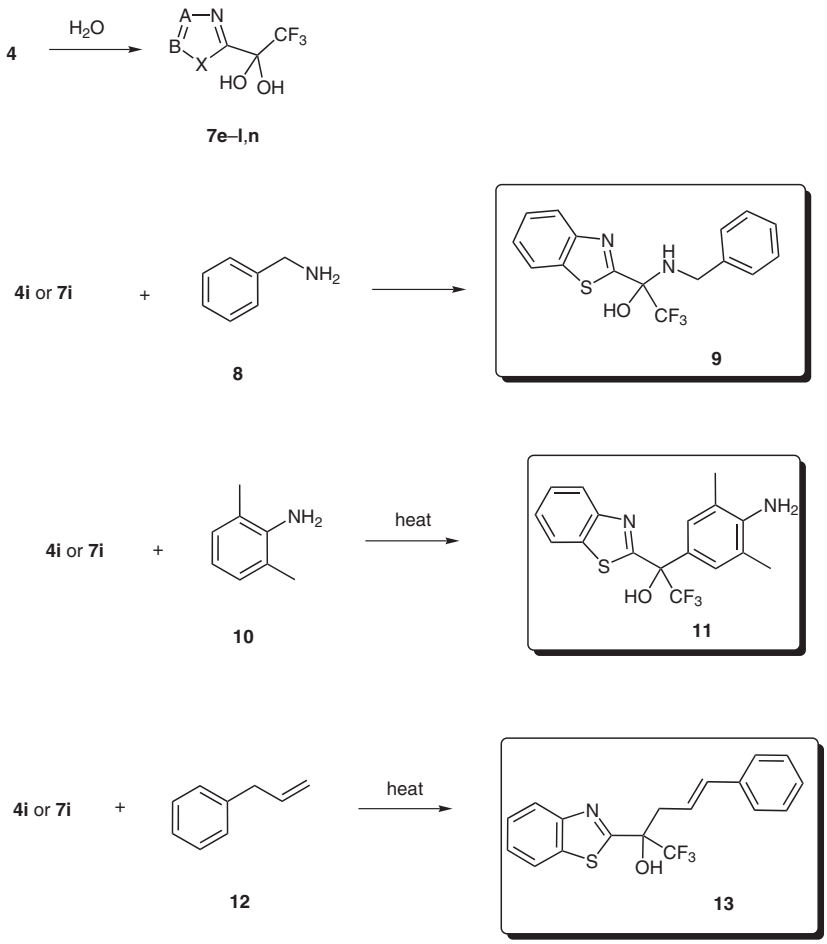


Scheme 3

Compounds **4** react with aliphatic amines to give stable *gem*-amino alcohols, e.g. **9** (Scheme 4), whereas the reactions with anilines afford unstable products, some of which rearrange into C-alkylated compounds, e.g. **11**, under heating (Scheme 4). At 156 °C the most electrophilic ketone **4i** underwent an ene reaction with allylbenzene (**12**) to give compound **13** in 64% yield.

The compositions and structures of all the compounds obtained were unambiguously established by mass spectrometry, elemental analysis, and NMR and IR spectroscopy. The ^{19}F NMR spectra of ketones **4** contain singlets between δ = –75.2 and –71.2 ppm. The fluorine atoms of hydrates **7** and alcohols **5** are, as expected, more strongly magnetically shielded, and this results in an upfield shift of their NMR signals into the range between δ = –83.7 and –81.9 ppm.

The structures of representative compounds **4m**, **5g**, and **7i** were confirmed by single-crystal X-ray analysis (Figures 1– 3). In the crystalline state, molecules **5g** form infinite chains stabilized by intermolecular hydrogen bonds between hydroxy groups and nitrogen atoms of the triazole fragments (Figure 2). Hydroxy groups of molecules **7i** in the crystalline state form intermolecular hydrogen bonds to the nitrogen atoms of the benzothiazole rings, resulting in infinite hydrogen-bonded tapes (Figure 3).



Scheme 4

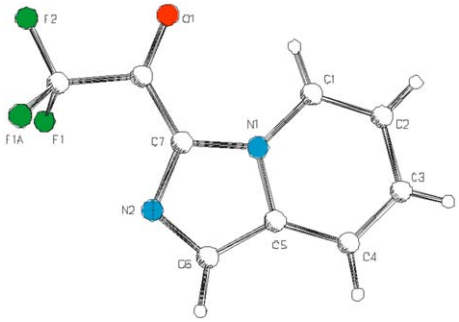


Figure 1 Molecular structure of compound **4n**

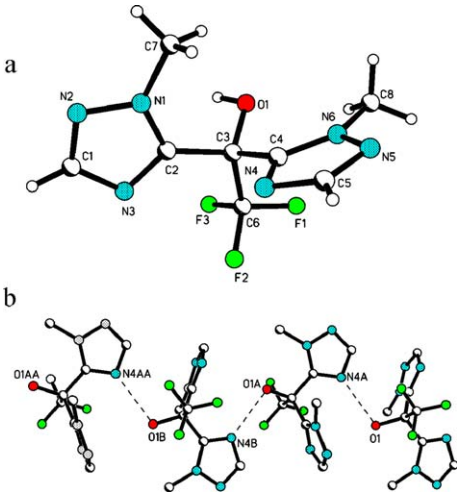


Figure 2 (a) Molecular and (b) crystal structures of compound **5g**

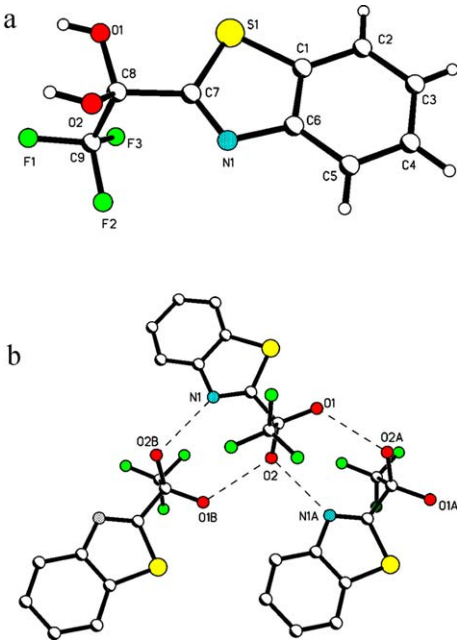


Figure 3 (a) Molecular and (b) crystal structures of compound **7i**

In conclusion, the reactions of imidazoles, 1,3-thiazoles, and 1,3-oxazoles with trifluoroacetic anhydride in the presence of triethylamine provide a facile method for the synthesis of heterocyclic trifluoromethyl-containing ketones. The chemical properties of the ketones bearing imidazole and benzimidazole fragments are similar to those of phenyl and methyl trifluoromethyl ketones, whereas the other ketones can be considered as analogues of trifluoropyruvate and hexafluoroacetone. The compounds form stable hydrates and aminals and, unlike common ketones, undergo noncatalytic ene reactions with terminal olefins, affording the corresponding allyl alcohols.

All commercially available azoles were purchased from Aldrich (**1a**, **1d**, **1f**, **1k**), Avocado (**1h**), Fluka (**1b**, **1c**), Hangzhou Pharma & Chem (**1e**), and Merck (**1i**), and were distilled prior to use. Compounds **1g**,[13] **1j**,[14] **1l**,[15] **1n**,[16] and **1p**[17] were prepared by literature procedures. Et_3N was distilled from $Phth_2O$ and KOH, and toluene and MeCN were distilled from P_2O_5. ^1H, ^{13}C, and ^{19}F NMR spectra of samples in $CDCl_3$ or DMSO-d_6 were recorded at r.t. on a Bruker Avance DRX 500 instrument. Mass spectra were recorded on an MX-1321 spectrometer (EI, 70 eV). Satisfactory microanalyses were obtained for all new substances: C, ±0.33; H, ±0.45; N, ±0.25.

2,2,2-Trifluoro-1-hetarylethanones 4 by Trifluoroacylation of Azoles 1; General Procedure

TFAA (2.52 g, 0.012 mol) was added dropwise (20 min) to a stirred soln of azole **1** (0.01 mol) in toluene (100 mL) at –19 °C. The addition of TFAA was generally accompanied with the precipitation of **2**, which readily dissolved on slow addition of Et_3N (1.21 g, 0.012 mol). After stirring for 6–8 h, the resulting yellow soln was slowly warmed to r.t. and left overnight. Removal of the solvent in vacuo, and treatment of the resulting oil with H_2O (sonication) gave hydrates **7**, which were converted into ketones **4** by distillation (Method A) or sublimation (Method B) under reduced pressure.

2,2,2-Trifluoro-1-(1-methyl-1*H*-imidazol-2-yl)ethanone (4a)

Method A: 88–92 °C (12 Torr); white crystals; yield: 82%; mp 56 °C.

IR (film): 3383, 3138, 3117, 3032, 1705, 1482, 1416, 1300, 1280, 1196, 1160, 948, 905, 798, 743, 675 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.07 (s, 3 H), 7.23 (s, 1 H), 7.37 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 36.3, 116.3 (q, $^1J_{CF}$ = 290.0 Hz), 129.3, 132.0, 138.0, 170.7 (q, $^2J_{CF}$ = 36.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.65.

MS (EI, 70 eV): *m*/*z* (%) = 178 (20) $[M]^+$, 109 (100) $[M – CF_3]^+$, 81 (7) $[M – COCF_3]^+$, 78 (13), 69 (25) $[CF_3]^+$, 54 (40), 52 (15), 42 (25), 40 (17), 32 (33).

2,2,2-Trifluoro-1-(1-vinyl-1*H*-imidazol-2-yl)ethanone (4b)

Method A: 114–115 °C (12 Torr); white crystals; yield: 75%; mp 54 °C.

IR (film): 3384 (br), 3137, 1672, 1647, 1464, 1413, 1279, 1205, 1171, 1092, 1063, 943, 903, 744 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.22 (dd, *J* = 8.7, 1.7 Hz, 1 H), 5.47 (dd, *J* = 15.6, 1.7 Hz, 1 H), 7.41 (s, 1 H), 7.59 (s, 1 H), 7.81 (dd, *J* = 15.6, 8.7 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 107.7, 116.2 (q, $^1J_{CF}$ = 290.0 Hz), 123.4, 130.0, 132.7, 136.8, 170.9 (q, $^2J_{CF}$ = 36.9 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.72.

MS (EI, 70 eV): *m*/*z* (%) = 190 (76) $[M]^+$, 121 (100) $[M – CF_3]^+$, 95 (12), 94 (95) $[M – COCF_3 + H]^+$, 79 (68), 69 (67) $[CF_3]^+$, 67 (25), 66 (15), 45 (57), 43 (20), 41 (59), 40 (42), 39 (31).

1-(1-Allyl-1*H*-imidazol-2-yl)-2,2,2-trifluoroethanone (4c)
Method A: 123–125 °C (12 Torr); white liquid; yield: 85%.

IR (film): 3381 (br), 3115, 2993 1701, 1647, 1467, 1414, 1311, 1275, 1228, 1203, 1161, 1074, 993, 955, 943, 904, 791, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.98 (d, *J* = 5.5 Hz, 2 H), 5.07 (d, *J* = 17 Hz, 1 H), 5.22 (d, *J* = 10 Hz, 1 H), 5.86–5.96 (m, 1 H), 7.28 (s, 1 H), 7.32 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 50.9, 116.4 (q, $^1J_{CF}$ = 290.5 Hz), 119.1, 128.2, 131.6, 132.2, 137.5, 170.4 (q, $^2J_{CF}$ = 36.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.62.

MS (EI, 70 eV): *m*/*z* (%) = 204 (14) $[M]^+$, 135 (38) $[M – CF_3]^+$, 107 (30), 41 (100), 39 (28).

1-(1-Butyl-1*H*-imidazol-2-yl)-2,2,2-trifluoroethanone (4d)
Method A: 160–162 °C (12 Torr); white crystals; yield: 77%; mp 32–33 °C.

IR (film): 3113 3101, 2965, 2860, 1699, 1475, 1412, 1275, 1223, 1204, 1161, 952, 904, 727, 669 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3 H), 1.35 (m, 2 H), 1.77 (m, 2 H), 4.41 (t, *J* = 7.5 Hz, 2 H), 7.27 (s, 1 H), 7.37 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 19.5, 32.8, 48.9, 116.4 (q, $^1J_{CF}$ = 290.0 Hz), 128.4, 132.1, 137.5, 170.4 (q, $^2J_{CF}$ = 36.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –71.26.

MS (EI, 70 eV): *m*/*z* (%) = 220 (23) $[M]^+$, 191 (15) $[M – C_2H_5]^+$, 178 (33) $[M – C_3H_6]^+$, 151 (65) $[M – CF_3]^+$, 123 (78) $[M – COCF_3]^+$, 95 (100) $[M – CF_3 – C_4H_8]^+$, 81 (25) $[M – C_3H_6 – COCF_3]^+$, 69 (46) $[CF_3]^+$, 57 (45), 56 (12), 41 (100), 40 (14).

1-(5-Chloro-1-methyl-1*H*-imidazol-2-yl)-2,2,2-trifluoroethanone (4e)
Method A: 107–108 °C (12 Torr); white crystals; yield: 83%; mp 68–69 °C.

IR (film): 3386 (br) 3120, 1701, 1475, 1415, 1394, 1286, 1196, 1163, 1103, 976, 899, 852, 744, 707 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.98 (s, 3 H), 7.30 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.1, 116.3 (q, $^1J_{CF}$ = 290.5 Hz), 128.2, 129.5, 137.5, 170.0 (q, $^2J_{CF}$ = 36.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.21.

MS (EI, 70 eV): *m*/*z* (%) = 214 (8) $[M + 2]^+$, 212 (33) $[M]^+$, 145 (26) $[M + 2 – CF_3]^+$, 143 (100) $[M – CF_3]^+$, 80 (34), 69 (11) $[CF_3]^+$, 42 (13).

2,2,2-Trifluoro-1-(1-methyl-1*H*-benzimidazol-2-yl)ethanone (4f)
Method B: 130–150 °C (0.5 Torr); white crystals; yield: 89%; mp 107–108 °C.

IR (film): 3048, 2954, 2913, 2848, 1723, 1458, 1218, 1173, 1156, 960, 748, 735 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.14 (s, 3 H), 7.41 (dd, *J* = 8.5, 7.0 Hz, 1 H), 7.46 (d, *J* = 8.5 Hz, 1 H), 7.52 (dd, *J* = 8.5, 7.0 Hz, 1 H), 7.97 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.2, 110.6, 116.2 (q, $^1J_{CF}$ = 290.1 Hz), 123.1, 124.8, 127.9, 136.9, 140.7, 142.4, 173.8 (q, $^2J_{CF}$ = 36.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.37.

MS (EI, 70 eV): *m*/*z* (%) = 229 (12) $[M + H]^+$, 228 (100) $[M]^+$, 160 (10), 159 (75) $[M – CF_3]^+$, 131 (21) $[M – COCF_3]^+$, 104 (17), 77 (33), 51 (13).

2,2,2-Trifluoro-1-(1-methyl-1*H*-1,2,4-triazol-5-yl)ethanone (4g)
Method A: 54–55 °C (12 Torr); colorless liquid; yield: 64%.

IR (film): 3448, 3130, 3026, 2966, 1740, 1492, 1475, 1416, 1371, 1300, 1286, 1205, 1171, 980, 928, 891, 783, 744, 715, 681 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.26 (s, 3 H), 8.08 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.1, 115.6 (q, $^1J_{CF}$ = 289.7 Hz), 144.1, 151.4, 171.4 (q, $^2J_{CF}$ = 39.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –75.21.

MS (EI, 70 eV): *m*/*z* (%) = 180 (9) $[M + H]^+$, 142 (31), 110 (100) $[M – CF_3]^+$, 83 (29) $[M – COCF_3 + H]^+$, 69 (20), 56 (26), 55 (11), 43 (17), 32 (30), 31 (17).

2,2,2-Trifluoro-1-(4-methyl-1,3-thiazol-2-yl)ethanone (4h)
Method A: 110–114 °C (12 Torr); yellow liquid; yield: 72%.

IR (film): 3113, 2983, 2933, 1712, 1499, 1432, 1338, 1209, 1192, 1164, 972, 881, 772, 725, 584 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.59 (s, 3 H), 7.47 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.2, 116.1 (q, $^1J_{CF}$ = 289.7 Hz), 124.5, 157.6, 158.4, 173.2 (q, $^2J_{CF}$ = 37.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.09.

MS (EI, 70 eV): *m*/*z* (%) = 195 (23) $[M]^+$, 126 (100) $[M – CF_3]^+$, 98 (12) $[M – COCF_3]^+$, 72 (8), 71 (46), 69 (25) $[CF_3]^+$, 45 (44), 39 (48), 32 (66), 31 (24).

1-(1,3-Benzothiazol-2-yl)-2,2,2-trifluoroethanone (4i)
Method B: 130–150 °C (0.5 Torr); yellow crystals; yield: 99%; mp 117–118 °C.

IR (film): 3064, 3031, 1716, 1478, 1340, 1212, 1161, 1125, 895, 725 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.67 (m, 2 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 8.30 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.0 (q, $^1J_{CF}$ = 290.3 Hz), 122.3, 126.7, 127.9, 129.3, 137.3, 153.7, 158.7, 175.1 (q, $^2J_{CF}$ = 37.9 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.91.

MS (EI, 70 eV): *m*/*z* (%) = 231 (56) $[M]^+$, 162 (100) $[M – CF_3]^+$, 134 (75) $[M – COCF_3]^+$, 90 (16), 78 (12), 69 (32) $[CF_3]^+$, 63 (16).

2,2,2-Trifluoro-1-(5-phenyl-1,3-oxazol-2-yl)ethanone (4j)
Method B: 130–140 °C (0.5 Torr); white crystals; yield: 80%; mp 76–77 °C.

IR (film): 3500–2900 (br), 1712, 1554, 1475, 1452, 1388, 1274, 1205, 1172, 1130, 1080, 999, 945, 916, 767, 746, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.57 (m, 3 H), 7.72 (s, 1 H), 7.78–787 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.9 (q, $^1J_{CF}$ = 288.8 Hz), 125.6, 125.7, 125.9, 129.4, 131.1, 152.6, 156.6, 167.1 (q, $^2J_{CF}$ = 39.4 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.24.

MS (EI, 70 eV): *m*/*z* (%) = 241 (100) $[M]^+$, 172 (74) $[M – CF_3]^+$, 116 (47), 105 (40), 89 (10), 77 (54), 69 (16) $[CF_3]^+$, 51 (16).

1-(1,3-Benzoxazol-2-yl)-2,2,2-trifluoroethanone (4k)
Method B: 130–140 °C (0.5 Torr); white crystals; yield: 65%; mp 93–94 °C.

IR (film): 3093, 3023, 1732, 1527, 1376, 1206, 1175, 1161, 1082, 981, 920, 737, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.7 Hz, 1 H), 7.64 (t, *J* = 7.7 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.1, 115.6 (q, $^1J_{CF}$ = 289.7 Hz), 123.4, 126.8, 130.5, 140.5, 150.8, 152.5, 169.7 (q, $^2J_{CF}$ = 39.9 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.95.

MS (EI, 70 eV): *m*/*z* (%) = 215 (26) $[M]^+$, 146 (100) $[M – CF_3]^+$, 119 (31), 102 (41), 91 (13), 90 (24), 78 (26), 69 (46) $[CF_3]^+$, 64 (50), 63 (36), 39 (21), 38 (13), 32 (25), 31 (28).

2,2,2-Trifluoro-1-(5-phenyl-1,3,4-thiadiazol-2-yl)ethanone (4l)
Method B: 140–150 °C (0.5 Torr); yellow crystals; yield: 56%; mp 108–109 °C.

IR (film): 3450–2850 (br), 1727, 1461, 1425, 1340, 1238, 1188, 1161, 1053, 898, 769, 692 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51–7.65 (m, 3 H), 8.07 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.7 (q, $^1J_{CF}$ = 289.7 Hz), 128.2, 128.8, 129.6, 133.1, 161.1, 173.5 (q, $^2J_{CF}$ = 39.8 Hz), 174.5.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.70.

MS (EI, 70 eV): *m*/*z* (%) = 258 (79) $[M]^+$, 189 (40) $[M – CF_3]^+$, 162 (15), 161 (34) $[M – COCF_3]^+$, 121 (13), 104 (20), 103 (100), 77 (37), 76 (12), 69 (36) $[CF_3]^+$, 51 (17).

2,2,2-Trifluoro-1-(imidazo[1,5-*a*]pyridin-3-yl)ethanone (4n)
Extracted from crude product with benzene; yellow crystals; yield: 75%; mp 142–143 °C.

IR (film): 3442 (br), 3072, 1641, 1461, 1371, 1362, 1263, 1207, 1176, 1146, 1124, 1093, 889, 763, 652 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (dd, *J* = 6.8 Hz, 1 H), 7.65 (dd, *J* = 8.8, 6.8 Hz, 1 H), 8.05 (s, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 9.52 (d, *J* = 6.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 117.0 (q, $^1J_{CF}$ = 289.3 Hz), 118.2, 118.5, 126.9, 127.1, 127.2, 130.5, 136.4, 168.1 (q, $^2J_{CF}$ = 36.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –72.73.

MS (EI, 70 eV): *m*/*z* (%) = 214 (81) $[M]^+$, 145 (100) $[M – CF_3]^+$, 117 (64) $[M – COCF_3]^+$, 90 (39), 69 (11) $[CF_3]^+$, 63 (22).

2,2,2-Trifluoro-1-(5-phenyl-1,3,4-oxadiazol-2-yl)ethanone (4p)
A soln of **6** (4.807 g, 22.02 mmol) in hexane (20 mL) was added dropwise to a stirred soln of TFAA (9.250 g, 6.22 mL, 44.04 mmol) in hexane (20 mL) at –30 °C. The reaction mixture was allowed to warm to r.t. and was stirred for 12 h. The precipitate that formed was collected by filtration and washed with hexane; this gave compound **4p**.

Yield: 3.430 g (64%); mp 128–130 °C.

IR (film): 3500–3000 (br), 1739, 1605, 1542, 1520, 1480, 1453, 1415, 1332, 1308, 1288, 1244, 1222, 1175, 1083, 1042, 1006, 938, 799, 745, 718, 695, 654, 627, 525, 476 cm^{-1}.

^{1}H NMR (500 MHz, benzene-d_6): δ = 6.92–7.06 (m, 3 H), 7.76 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, benzene-d_6): δ = 115.9 (q, $^1J_{CF}$ = 289.0 Hz), 122.5, 128.2, 129.3, 133.3, 157.5, 167.0, 167.3 (q, $^2J_{CF}$ = 31.2 Hz).

^{19}F NMR (470 MHz, benzene-d_6): δ = –74.8.

MS (EI, 70 eV): *m*/*z* (%) = 242 (31) $[M]^+$, 146 (11), 145 (81), 105 (8), 103 (32), 89 (5), 78 (6), 77 (100), 76 (11), 69 (21) $[CF_3]^+$, 63 (11), 59 (6), 51 (19), 50 (12), 39 (9), 31 (39), 30 (51).

2,2,2-Trifluoro-1,1-bis(hetaryl)ethanols 5; General Procedure
TFAA (0.01 mol) was added dropwise to a stirred soln of the appropriate azole **1** (0.01 mol) and Et_3N (0.01 mol) in MeCN (20 mL) at 0 °C. The reaction mixture was warmed to r.t., then stirred for 3 h, and subsequently treated with H_2O (20 mL). The precipitate was collected by filtration, washed with aq EtOH and recrystallized from *i*-PrOH.

2,2,2-Trifluoro-1,1-bis(1-methyl-1*H*-benzimidazol-2-yl)ethanol (5f)
White crystals; yield: 78%; mp 195–196 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.71 (s, 6 H), 7.27 (dd, *J* = 8.0, 7.2 Hz, 2 H), 7.35 (dd, *J* = 8.0, 7.2 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 8.74 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 32.0, 76.6 (q, $^2J_{CF}$ = 30.2 Hz), 111.0, 120.2, 122.7, 123.9, 124.6 (q, $^1J_{CF}$ = 288.0 Hz), 136.9, 141.5, 148.2.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –74.02.

MS (EI, 70 eV): *m*/*z* (%) = 361 (11), 360 (83) $[M]^+$, 359 (38), 292 (12), 291 (69) $[M – CF_3]^+$, 263 (24), 229 (24), 159 (56), 146 (100), 145 (13), 133 (25), 132 (100), 131 (89), 104 (21), 90 (10), 77 (34).

2,2,2-Trifluoro-1,1-bis(1-methyl-1*H*-1,2,4-triazol-5-yl)ethanol (5g)
White crystals; yield: 18%; mp 166–168 °C (sublimed).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.77 (s, 6 H), 8.00 (s, 2 H), 8.97 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 37.8, 73.6 (q, $^2J_{CF}$ = 31.3 Hz), 124.0 (q, J_{CF} = 288.0 Hz), 149.4, 150.2.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –76.80.

2,2,2-Trifluoro-1,1-bis(4-methyl-1,3-thiazol-2-yl)ethanol (5h)
Brown crystals; yield: 6%; mp 141–142 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.38 (s, 6 H), 7.41 (s, 2 H), 8.77 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 17.3, 77.7 (q, $^2J_{CF}$ = 30.2 Hz), 117.7, 123.7 (q, $^1J_{CF}$ = 289.2 Hz), 152.9, 165.9.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –75.75.

MS (EI, 70 eV): *m*/*z* (%) = 294 (16) $[M]^+$, 225 (74) $[M – CF_3]^+$, 196 (21), 126 (100), 99 (25), 72 (12), 71 (32), 45 (32), 39 (21).

1,1-Bis(1,3-benzothiazol-2-yl)-2,2,2-trifluoroethanol (5i)
White crystals; yield: 67%; mp 138–139 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.42–7.58 (m, 4 H), 8.02–8.12 (m, 4 H), 9.12 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 78.2 (q, $^2J_{CF}$ = 29.5 Hz), 122.6, 123.2 (q, $^1J_{CF}$ = 288.7 Hz), 123.6, 126.3, 126.8, 135.0, 152.3, 167.4.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –74.10.

MS (EI, 70 eV): *m*/*z* (%) = 366 (67) $[M]^+$, 297 (80) $[M – CF_3]^+$, 269 (26), 232 (44), 162 (100), 135 (60), 134 (69), 108 (26), 69 (21) $[CF_3]^+$, 32 (13).

Hydrates 7; General Procedure
A soln of the appropriate ketone **4** in benzene in an open vial was placed in a cold water bath and left overnight. The precipitate was collected by filtration, washed with benzene, and dried in the open air. The yields were almost quantitative.

1-(5-Chloro-1-methyl-1*H*-imidazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (7e)
White crystals; mp 100–120 °C (sublimed).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.69 (s, 3 H), 7.02 (s, 1 H), 7.96 (br s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 32.5, 90.8 (q, $^2J_{CF}$ = 32.7 Hz), 120.6, 123.1 (q, $^1J_{CF}$ = 289.2 Hz), 123.5, 142.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –83.42.

MS (EI, 70 eV): *m*/*z* (%) = 230 (95) $[M]^+$, 212 (17) $[M – H_2O]^+$, 161 (17) $[M – CF_3]^+$, 143 (100) $[M – CF_3 – H_2O]^+$, 80 (25), 74 (10), 69 (13) $[CF_3]^+$, 42 (17).

2,2,2-Trifluoro-1-(1-methyl-1*H*-benzimidazol-2-yl)ethane-1,1-diol (7f)
White crystals; mp 129–137 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.97 (s, 3 H), 7.26 (dd, *J* = 7.5 Hz, 1 H), 7.34 (dd, *J* = 7.5 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 8.21 (br s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 32.2, 91.4 (q, $^2J_{CF}$ = 33.5 Hz), 111.1, 119.8, 122.3 (q, $^1J_{CF}$ = 289.0 Hz), 123.1, 124.3, 136.8, 140.3, 149.0.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –81.97.

MS (EI, 70 eV): *m*/*z* (%) = 246 (0.4) $[M]^+$, 229 (13), 228 (100) $[M – H_2O]^+$, 177 (0.5) $[M – CF_3]^+$, 159 (96) $[M – H_2O – CF_3]^+$, 132 (11), 131 (16), 104 (17), 77 (32), 69 (42) $[CF_3]^+$, 51 (24), 50 (10), 45 (50).

2,2,2-Trifluoro-1-(1-methyl-1*H*-1,2,4-triazol-5-yl)ethane-1,1-diol (7g)
White crystals; mp 122–128 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.98 (s, 3 H), 7.94 (s, 1 H), 8.31 (br s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 37.9, 90.4 (q, $^2J_{CF}$ = 33.2 Hz), 122.8 (q, $^1J_{CF}$ = 289.3 Hz), 149.5, 151.1.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –82.68.

MS (EI, 70 eV): *m*/*z* (%) = 179 (5) $[M – H_2O]^+$, 128 (37) $[M – CF_3]^+$, 110 (100) $[M – CF_3 – H_2O]^+$, 83 (13), 69 (12) $[CF_3]^+$, 56 (15), 43 (12).

2,2,2-Trifluoro-1-(4-methyl-1,3-thiazol-2-yl)ethane-1,1-diol (7h)
White crystals; mp 98–102 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.43 (s, 3 H), 7.16 (s, 1 H), 7.90 (s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 17.0, 91.7 (q, $^2J_{CF}$ = 32.2 Hz), 116.9, 122.8 (q, $^1J_{CF}$ = 289.3 Hz), 152.7, 167.2.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –83.36.

MS (EI, 70 eV): *m*/*z* (%) = 213 (7) $[M]^+$, 195 (20) $[M – H_2O]^+$, 144 (17) $[M – CF_3]^+$, 126 (100) $[M – H_2O – CF_3]^+$, 98 (12) $[M – H_2O – COCF_3]^+$, 72 (13), 71 (48), 69 (17) $[CF_3]^+$, 45 (34), 39 (33), 32 (28).

1-(1,3-Benzothiazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (7i)
White crystals; mp 104–111 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.50 (t, *J* = 7.9 Hz, 1 H), 7.56 (t, *J* = 7.9 Hz, 1 H), 8.09 (d, *J* = 7.9 Hz, 1 H), 8.15 (d, *J* = 7.9 Hz, 1 H), 8.48 (s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 92.0 (q, $^2J_{CF}$ = 32.5 Hz), 122.6, 122.8 (q, $^1J_{CF}$ = 289.7 Hz), 123.6, 126.1, 126.6, 135.3, 152.9, 169.5.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –82.24.

MS (EI, 70 eV): *m*/*z* (%) = 249 (1) $[M]^+$, 231 (77) $[M – H_2O]^+$, 162 (100) $[M – H_2O – CF_3]^+$, 134 (76) $[M – H_2O – COCF_3]^+$, 107 (15), 69 (30) $[CF_3]^+$, 63 (15).

2,2,2-Trifluoro-1-(5-phenyl-1,3-oxazol-2-yl)ethane-1,1-diol (7j)
White crystals; mp 99–103 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.40 (t, *J* = 7.5 Hz, 1 H), 7.49 (dd, *J* = 7.5 Hz, 2 H), 7.75 (d, *J* = 7.5 Hz, 2 H), 7.77 (s, 1 H), 8.38 (br s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 90.2 (q, $^2J_{CF}$ = 33.5 Hz), 122.9 (q, $^1J_{CF}$ = 289.2 Hz), 123.1, 124.7, 127.5, 129.5, 129.6, 152.1, 159.0.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –82.99.

MS (EI, 70 eV): *m*/*z* (%) = 259 (3) $[M]^+$, 242 (16), 241 (100) $[M – H_2O]^+$, 172 (92) $[M – H_2O – CF_3]^+$, 116 (87), 105 (70), 89 (25), 77 (91), 69 (31) $[CF_3]^+$, 63 (12), 51 (33), 50 (15), 39 (15).

1-(1,3-Benzoxazol-2-yl)-2,2,2-trifluoroethane-1,1-diol (7k)
White crystals; mp 110–115 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.36–7.46 (m, 2 H), 7.68–7.72 (d, 1 H), 7.76–7.80 (d, 1 H), 8.24 (s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 90.1 (q, $^2J_{CF}$ = 33.2 Hz), 111.4, 120.6, 122.3 (q, J_{CF} = 289.0 Hz), 125.1, 126.4, 139.9, 150.1, 161.0.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –82.51.

MS (EI, 70 eV): *m*/*z* (%) = 233 (20) $[M]^+$, 215 (50) $[M – H_2O]^+$, 164 (17) $[M – CF_3]^+$, 146 (100) $[M – H_2O – CF_3]^+$, 119 (67), 102 (31), 92 (10), 91 (47), 90 (27), 69 (42) $[CF_3]^+$, 64 (68), 63 (50), 39 (21)

2,2,2-Trifluoro-1-(5-phenyl-1,3,4-thiadiazol-2-yl)ethane-1,1-diol (7l)
White crystals; mp 111–116 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.50–7.60 (m, 3 H), 8.00 (d, *J* = 6.5 Hz, 2 H), 8.78 (br s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 91.8 (q, $^2J_{CF}$ = 33.5 Hz), 122.9 (q, $^1J_{CF}$ = 289.2 Hz), 128.2, 129.7, 130.0, 132.1, 169.6, 170.5.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –83.65.

MS (EI, 70 eV): *m*/*z* (%) = 276 (3) $[M]^+$, 258 (68) $[M – H_2O]^+$, 207 (4) $[M – CF_3]^+$, 189 (52) $[M – H_2O – CF_3]^+$, 161 (46) $[M – H_2O – COCF_3]^+$, 121 (16), 103 (100), 77 (35), 76 (15), 69 (41) $[CF_3]^+$, 63 (11), 51 (23), 50 (14).

2,2,2-Trifluoro-1-(5-phenyl-1,3,4-oxadiazol-2-yl)ethane-1,1-diol (7p)
White crystals; mp 114 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.63–7.71 (m, 3 H), 8.04 (d, *J* = 7.1 Hz, 2 H), 8.80 (s, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 89.4 (q, $^2J_{CF}$ = 34.0 Hz), 121.9 (q, $^1J_{CF}$ = 289.0 Hz), 122.6, 126.7, 129.6, 132.5, 162.7, 164.8.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –83.00.

1-(1,3-Benzothiazol-2-yl)-1-(benzylamino)-2,2,2-trifluoroethanol (9)
A mixture of **4i** (1 equiv) and $BnNH_2$ (**8**; 1 equiv) in toluene was heated for 5 min. The precipitate that formed was crystallized from *i*-PrOH.

Yield 77%; mp 96–97 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.62 (m, 1 H), 3.82–3.94 (m, 2 H), 7.20 (t, *J* = 7.0 Hz, 1 H), 7.28 (dd, *J* = 7.0 Hz, 2 H), 7.36 (d, *J* = 7.0 Hz, 2 H), 7.50 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.56 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.92 (br s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 45.4, 86.4 (q, $^2J_{CF}$ = 29.8 Hz), 122.9, 123.8, 124.0 (q, $^1J_{CF}$ = 290.5 Hz), 126.3, 126.9, 127.2, 128.4, 128.5, 136.1, 140.3, 153.2, 170.0.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –78.89.

1-(4-Amino-3,5-dimethylphenyl)-1-(1,3-benzothiazol-2-yl)-2,2,2-trifluoroethanol (11)

A mixture of **4i** (1 equiv) and 2,6-dimethylaniline (**10**; 1 equiv) in toluene was heated for 3 h at 100 °C. The precipitate that formed was crystallized from *i*-PrOH.

Beige crystals; yield: 25%; mp 222–223 °C

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.05 (s, 6 H), 4.77 (s, 2 H), 7.10 (s, 2 H), 7.46 (dd, *J* = 6.5 Hz, 1 H), 7.53 (dd, *J* = 6.5 Hz, 1 H), 8.08 (m, 3 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 18.6, 78.3 (q, $^2J_{CF}$ = 28.9 Hz), 120.4, 122.7, 123.3, 123.8, 125.0 (q, $^1J_{CF}$ = 288.0 Hz), 126.1, 126.8, 126.8, 135.0, 145.5, 153.2, 173.0.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –75.88.

MS (EI, 70 eV): *m*/*z* (%) = 352 (22) $[M]^+$, 283 (39) $[M – CF_3]^+$, 162 (13), 119 (10), 148 (100), 136 (17), 120 (16).

2-(1,3-Benzothiazol-2-yl)-1,1,1-trifluoro-5-phenylpent-4-en-2-ol (13)

A mixture of **4i** (1 equiv) and allylbenzene (**12**; 3 equiv) was heated in a pressure tube for 24 h at 130 °C. Excess **12** was then removed at reduced pressure, and the product was purified by flash chromatography.

Brown oil; yield: 64%.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.04–3.14 (m, 1 H), 3.20–3.30 (m, 1 H), 6.00–6.14 (m, 1 H), 6.48 (d, *J* = 15.6 Hz, 1 H), 7.10–7.32 (m, 5 H), 7.46 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.53 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.90 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.0 Hz, 1 H)

^{13}C NMR (125 MHz, DMSO-d_6): δ = 38.66, 77.88 (q, $^2J_{CF}$ = 27.7 Hz), 121.94, 122.79, 123.63, 125.12 (q, $^1J_{CF}$ = 288.0 Hz), 125.99, 126.38, 126.80, 127.92, 129.04, 134.85, 135.31, 137.03, 153.60, 171.19.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –78.16.

Single-Crystal X-ray Analyses

Unit cell parameters and intensities of all sets of reflections were measured on an Xcalibur-3 diffractometer (CCD detector, λ(MoKα) irradiation, ω-scans) All structures were solved by direct methods by use of the SHELXTL package.[18] Positions of the hydrogen atoms were located from difference maps of the electron density and refined within isotropic approximation (**4n**, **7i**) or by use of a riding model (**5j**). Atomic coordinates and crystallographic parameters were deposited at the Cambridge Crystallographic Data Centre under CCDC 662987-662989.

Crystal Data for 4n

$C_9H_5N_2OF_3$, monoclinic, $P2_1/m$, *a* = 8.001(1) Å, *b* = 6.699(1) Å, *c* = 8.262(1) Å, β = 93.98(1)°, *V* = 441.69(4) Å^3, *Z* = 2, ρ_{calcd} = 1.61 g/cm^3, μ = 0.151 mm^{-1}, *F*(000) = 216, 103 parameters, R_1 = 0.038, wR_2 = 0.1077 (779 reflections, $F > 4\sigma$), R_1 = 0.052, wR_2 = 0.1155 (1092 unique reflections), *S* = 1.144, Δρ (min/max) = –0.151/0.163 e Å^{-3}.

Crystal Data for 5g

$C_8H_9N_6OF_3$, monoclinic, $P2_1/n$, *a* = 9.6712(3) Å, *b* = 10.3909(3) Å, *c* = 11.4583(4) Å, β = 100.10(1)°, *V* = 1133.63(6) Å^3, *Z* = 4, ρ_{calcd} = 1.536 g/cm^3, μ = 0.142 mm^{-1}, *F*(000) = 536, 169 parameters, R_1 = 0.039, wR_2 = 0.090 (1481 reflections, $F > 4\sigma$), R_1 = 0.0785, wR_2 = 0.1032 (2529 unique reflections), *S* = 0.893, Δρ (min/max) = –0.164/0.216 e·Å^{-3}.

Crystal data for 7i

$C_9H_6NO_2SF_3$, orthorhombic *Pbca*, *a* = 13.235(1) Å, *b* = 7.734(1) Å, *c* = 18.735(1) Å, *V* = 1917.6(1) Å^3, *Z* = 8, ρ_{calcd} = 1.726 g/cm^3, $\mu(MoK_\alpha)$ = 0.366 mm^{-1}, *F*(000) = 1008, 163 parameters, R_1 = 0.033, wR_2 = 0.075 (1637 reflections, $F > 4\sigma$), R_1 = 0.068, wR_2 = 0.084 (2707 unique reflections), *S* = 0.880, Δρ (min/max) = –0.175/0.268 e·Å^{-3}.

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